NO_x Control Options and Integration for US Coal Fired Boilers

Quarterly Progress Report

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Abstract

This is the eighteenth Quarterly Technical Report for DOE Cooperative Agreement No: DE-FC26-00NT40753. The goal of the project is to develop cost effective analysis tools and techniques for demonstrating and evaluating low NO_x control strategies and their possible impact on boiler performance for boilers firing US coals. The Electric Power Research Institute (EPRI) is providing co-funding for this program. Safety equipment for ammonia for the SCR slipstream reactor at Plant Gadsden was installed. The slipstream reactor was started and operated for about 1400 hours during the last performance period. Laboratory analysis of exposed catalyst and investigations of the sulfation of fresh catalyst continued at BYU. Thicker end-caps for the ECN probes were designed and fabricated to prevent the warpage and failure that occurred at Gavin with the previous design. A refurbished ECN probe was successfully tested at the University of Utah combustion laboratory. Improvements were implemented to the software that controls the flow of cooling air to the ECN probes.

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Executive Summary

The work to be conducted in this project received funding from the Department of Energy under Cooperative Agreement No: DE-FC26-00NT40753. This project has a period of performance that started February 14, 2000 and continues through March 31, 2005.

Our program contains five major technical tasks:

- evaluation of Rich Reagent Injection (RRI) for in-furnace NO_x control;
- demonstration of RRI technologies in full-scale field tests at utility boilers;
- impacts of combustion modifications (including corrosion and soot);
- ammonia adsorption / removal from fly ash; and
- SCR catalyst testing.

To date, good progress is being made on the overall program. We have seen considerable interest from industry in the program due to our successful initial field tests of the RRI technology and the corrosion monitor.

During the last three months, our accomplishments include the following:

- Safety equipment for ammonia was installed for the SCR slipstream reactor at Plant Gadsden. The reactor accumulated ~1400 hours of operation during the last performance period. A preliminary assessment of NO_x activity was made.
- Laboratory analysis of exposed catalyst and investigations of the sulfation of fresh catalyst continued at BYU.
- Thicker end-caps for the ECN probes were designed and fabricated to prevent the warpage and failure that occurred at Gavin with the previous design. One refurbished ECN probe was successfully tested at the University of Utah combustion laboratory.
- Improvements to the software that controls the flow of cooling air to the ECN probes were implemented.
- The refurbished ECN probes and improved controller software will be re-installed at Gavin next quarter.

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Experimental Methods

Within this section we present in order, brief discussions on the different tasks that are contained within this program. For simplicity, the discussion items are presented in the order of the tasks as outlined in our original proposal.

Task 1 - Program Management

During the last performance period,

- Corrosion Probe:
  - Thicker end-caps for the corrosion probes were designed and fabricated. One corrosion probe with the thicker end-cap was tested at the University of Utah combustion laboratory for three days. The cyclical heating/cooling behavior that led to the failure of the end-caps at Gavin was not observed.
  - Refurbishment of the probes will be completed and the corrosion probes re-installed at Gavin next quarter.
  - Improvements to the software that controls the flow of cooling air to the corrosion probes have been implemented and will be tested during the re-installation of the probes at Gavin next quarter.
- SCR:
  - At Gadsden, safety equipment for ammonia was installed, the reactor successfully started and was operational for a total of ~1400 hours. A preliminary assessment of NO_x activity was made.
  - Laboratory investigations at BYU of the catalysts exposed for 2000 hours to flue gas indicated that the activity of these samples was essentially unchanged (possibly slightly increased) relative to the activity of the fresh, unexposed samples. Preliminary data (not yet graphed) with catalysts exposed for longer times (3800 hours) indicated that catalyst activity decreases relative to the fresh samples and those exposed for 2000 hours.
  - In situ spectroscopic data indicate that sulfation of the catalyst increases activity significantly (by 50% or more). Sulfation primarily leads to an increase in adsorbed ammonia, which in turn would lead to increased reaction between NO and adsorbed ammonia.

During the last performance period, REI was recommended for award of a DOE-funded project entitled, "Pilot Scale Demonstration of Advanced Layered NO_x Control Technology For Coal-Fired Boilers". Subject to final negotiation, the project is scheduled to start Spring, 2005. In the project, REI would work with the University of Utah (which would provide testing services) and EPRI (which would provide cost share). The goal of the project is to develop and verify the performance of a fundamentally different burner design for NOx control. If successful, the new burner design will create homogeneous combustion products in the boiler, which are ideal conditions for combustion-related NOx control and results in stoichiometry and temperature distributions above the burners that is ideal for use of Rich Reagent Injection (RRI), an in-furnace NO_x control technology demonstrated early within this project. REI will perform computational modeling and conduct pilot-scale testing at the University of Utah to evaluate and

optimize the burner design and reagent injection strategy. In addition, modeling will be performed to demonstrate the potential for NOx reduction in a full-scale boiler.

During the last performance period two power industry companies have awarded projects to REI to use the Corrosion Monitoring System, a technology which is being evaluated within this project, for R&D programs at their sites. The projects involve a 1.5 MW coal-fired pilot-scale furnace and a coal-fired 100 MMBTU/hr single burner test facility.

Industry Involvement

A paper co-authored by REI and electric utility personnel was presented at an engineering conference that highlighted the RRI NOx control technology demonstrated earlier within this project:

- Cremer, M.A., Wang, D.H., Adams, B.R., Boll, D.E., and Stuckmeyer, K.B. "Evaluation of Cost Effective Non-SCR Options For NOx Control in PRB Fired Cyclone Boilers," presented at the 19th International Conference on Lignite, Brown, and Subbituminous Coals, Billings, MT, October 12-14, 2004.

A paper was presented at an engineering conference that highlighted results from measurements of mercury oxidation across the SCR slipstream unit used within this project:

- Senior, C.L., "Understanding Oxidation of Mercury Across SCR Catalysts in Power Plants Burning Low Rank Coals," presented at the Power-Gen International Conference, November 29-December 1, 2004, Orlando, Florida

Task 3 - Minimization of Impacts

Corrosion probes were reinstalled at Gavin station at the end of August, but were found to experience temperature control irregularities not previously seen at Gavin or the previous boiler installations at B.L. England and Eastlake stations. Analysis of the sensor temperature data showed that the individual temperatures were fluctuating severely every second. This fluctuation in the temperatures not only resulted in the unstable corrosion measurement, but also caused the cooling air to shut-off, turn on full blast, shut-off, turn on, etc. This did not permit adequate cooling of the probe.

As a result of this instability, the corrosion probes were again damaged in mid-September and have been removed and are being refurbished. It appeared from these probes that the probe cap was machined too thin and severe warpage occurred. This has been corrected with the design of a thicker end cap. The new cap was installed on a probe and tested in the University of Utah combustion facility for three days. It performed flawlessly. All remaining end caps are being machined now.

Improvements have also been made to the control system and control parameters used for the cooling air. These new methods will be tried with one probe at Gavin as early as feasible in January and then on all probes when they are reinstalled in late January.
Testing at Gavin is scheduled to be completed the first week of April when the unit is scheduled for an outage.

Task 4 - SCR Catalyst Testing

Selective catalytic reduction (SCR) represents the only commercially proven technology capable of achieving the relatively large NO_x reductions required to comply with the latest (amended) Clean Air Act requirements. SCR systems are being installed in most large-scale utility boilers. However, most long-term experience with SCR comes from Germany and Japan and most of this is based on high-rank coal combustion. Less experience with low-rank, subbituminous coals specifically Powder River Basin coals, appears in the literature. The literature also provides essentially no US and little foreign experience with systems co-fired with biomass. The purpose of this task is to provide both laboratory and field slipstream data and analyses, including computer models that fill this information gap.

Within this task there are for principal sub-tasks:
1. technology assessment and fundamental analysis of chemical poisoning of SCR catalysts by alkali and alkaline earth materials;
2. evaluation of commercial catalysts in a continuous flow system that simulates commercial operation;
3. evaluating the effectiveness of catalyst regeneration; and
4. develop a model of deactivation of SCR catalysts suitable for use in a CFD code.

Items 1 and 3 are principally performed at Brigham Young University (BYU) under the direction of Profs. Larry Baxter, Calvin Bartholomew, and William Hecker. The work effort for items 2 and 4 is being performed by REI, with assistance from the University of Utah and BYU. Progress during the last performance period on this task is described below.

Task 4.1 Technology Assessment/Fundamental Analysis

Tests of Monolith Catalysts from REI Slipstream Reactor

Tests on both fresh and 2063-hour-exposed samples from commercial monolith catalysts, M1, M2, and M3 completed this quarter indicate that catalyst activity over this period is unchanged or slightly increased relative to fresh catalysts. All samples taken from the exposed catalysts came from the upstream end where impact of ash and contaminants should be the greatest. Sample sizes appear in Table 1. The catalyst-gas area was relatively consistent from sample to sample for M1 and M2, but the area varied significantly for M3 due to the non-rectangular, wave-like nature of the M3 cross sections.

Table 1: Sample Sizes.

CATALYST	LENGTH (cm)	WIDTH (cm)	HEIGHT (cm)
M1	3.1	1.5	1.5
M2	2.9	1.4	1.4
M3	3.2	1.5	1.7

The monolith reactor provided temperature and flow control for tests on each sample. The reactor maintained 1000 sccm gas flow consisting of 2% O_2, 10% H_2O, 900 ppm NH_3, 900 ppm NO, and the balance He. The reactor temperature varied from 250 ^oC to 325 ^oC in increments of 25 ^oC for each sample.

Figure 1 shows a comparison of NO conversion for the fresh versus exposed M1 catalyst as a function of reactor temperature. Figure 2 shows the same comparison for the M2 catalyst. Both figures include 90% confidence intervals for the measured values based on variances determined by replicated measurements. Regions of non-overlapping confidence bands indicate the statistically most significant differences in the measured results. As indicated, the catalysts exhibit nearly the same activity over the entire temperature range, with the greatest difference – which is marginally statistically significant – at the lowest temperatures. Therefore, both data sets indicate that flue-gas exposure did not decrease catalyst activity over this relatively short time. In fact, activity slightly increases for the exposed catalyst at temperatures below 270^oC. As catalyst temperature decreases, reaction kinetics play an increasingly larger role in determining conversion. As temperature increases, and especially at high conversions, transport of gases to and from the catalyst surface increasingly influences observed conversion, and kinetics plays a less significant role. These data suggest that kinetic activity remained either unaffected or slightly increased for these samples. This is consistent with the more detailed kinetic analyses from the in situ spectroscopic lab. These detailed kinetic analyses indicate that sulfation of the catalyst leads to an overall slight increase in catalyst reactivity, even though it appears to be the titania substrate and not the vanadium sites that sulfate.

Figure 3 shows a similar preliminary comparison for M3. The current data for M3 varies more than that for M1 and M2. The current hypothesis is that this is due to more variation in the surface area of the samples, which is much more difficult to control for catalysts of M3 design than for traditional monolith catalysts with rectangular channels. While the data indicate the same general conclusion, that there is little difference between exposed and fresh catalyst, the data scatter is much larger. Data with less scatter and a more complete discussion of the techniques should appear in the next report.

Similar tests performed on M1, M2, and M3 samples from the last series of tests (3800 hours of exposure in a slipstream reactor) are underway. Preliminary results from these tests show that these catalysts have experienced a decrease in apparent activity, but the decrease is more consistent with fouling of the surface than with chemical poisoning. Based on these preliminary data, the overall conclusion from these investigations indicates the following SCR response to low-rank coals: The typically un-sulfated fresh catalysts initially increase in activity slightly as the surfaces sulfate in the SO_2-laden flows. In these experiments, this slight increase is apparent up to about 2000 hours of exposure. Accumulation of presumably fine ash particles eventually overcomes the sulfate-based activity enhancement and leads to slight decreases in activity during

longer exposures (> 2000 hours), with activity changes noticeable at 3800 hours. No data suggest that chemical poisoning of the catalyst surface in a manner that changes kinetic activation energies is operative. The decrease appears to be associated with a decrease in surface availability, possibly due to pore blockage by fouling ash material on the SCR surface. A more complete analysis of these data will be included in the next report.

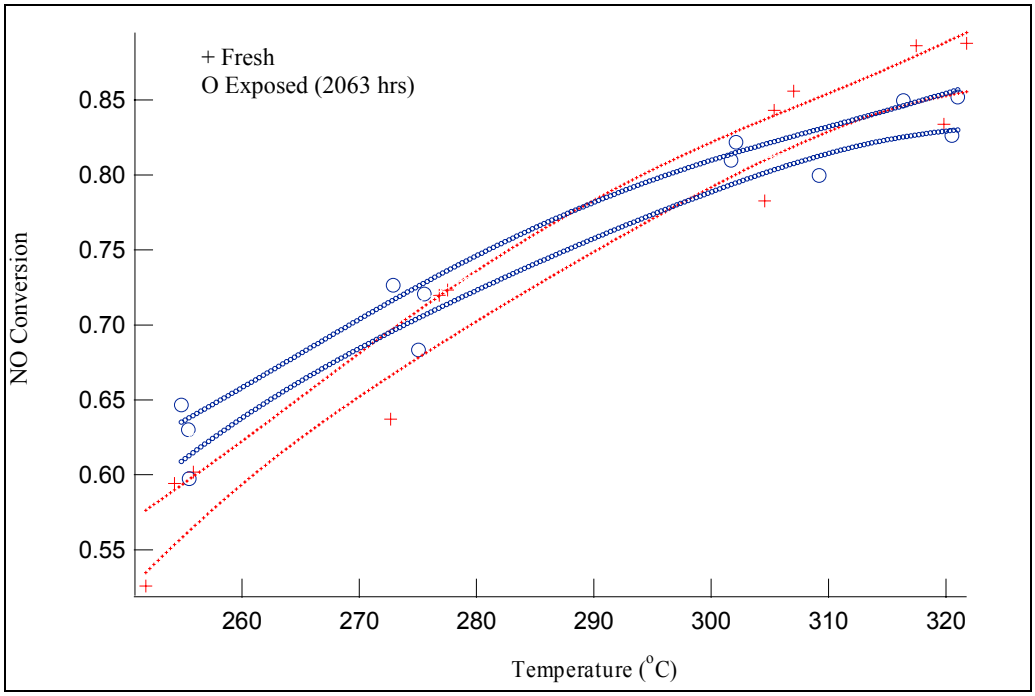

Figure 1. M1 results with 90% confidence bands.

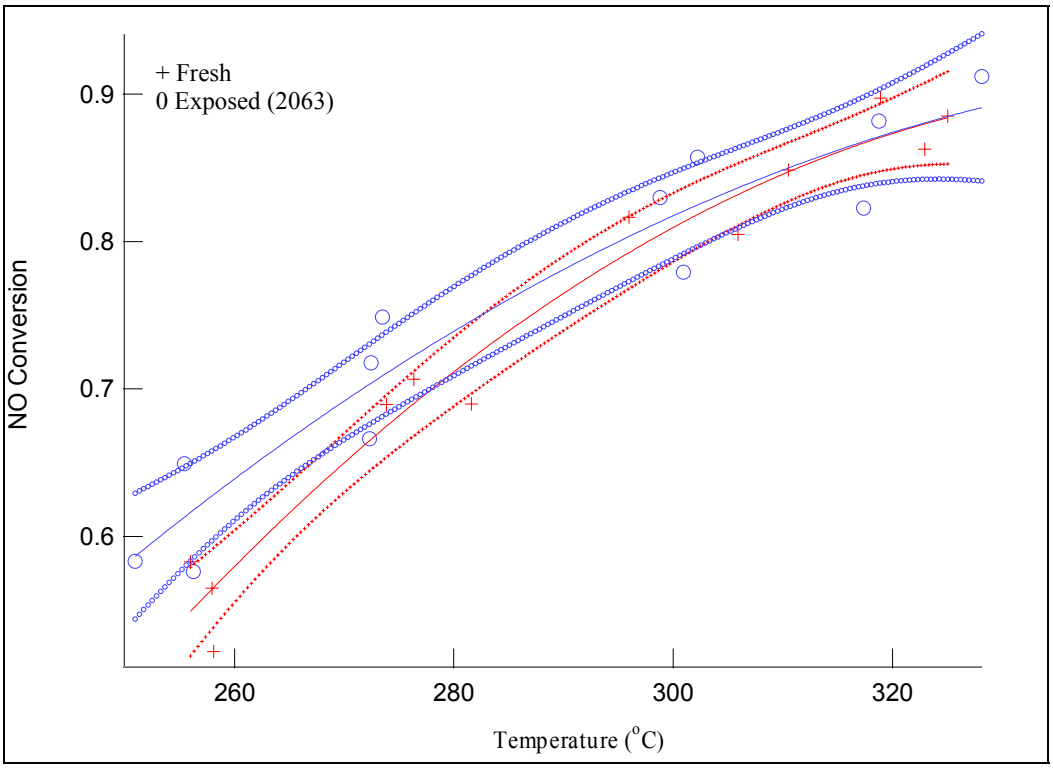

Figure 2. M2 results with 90% confidence bands.

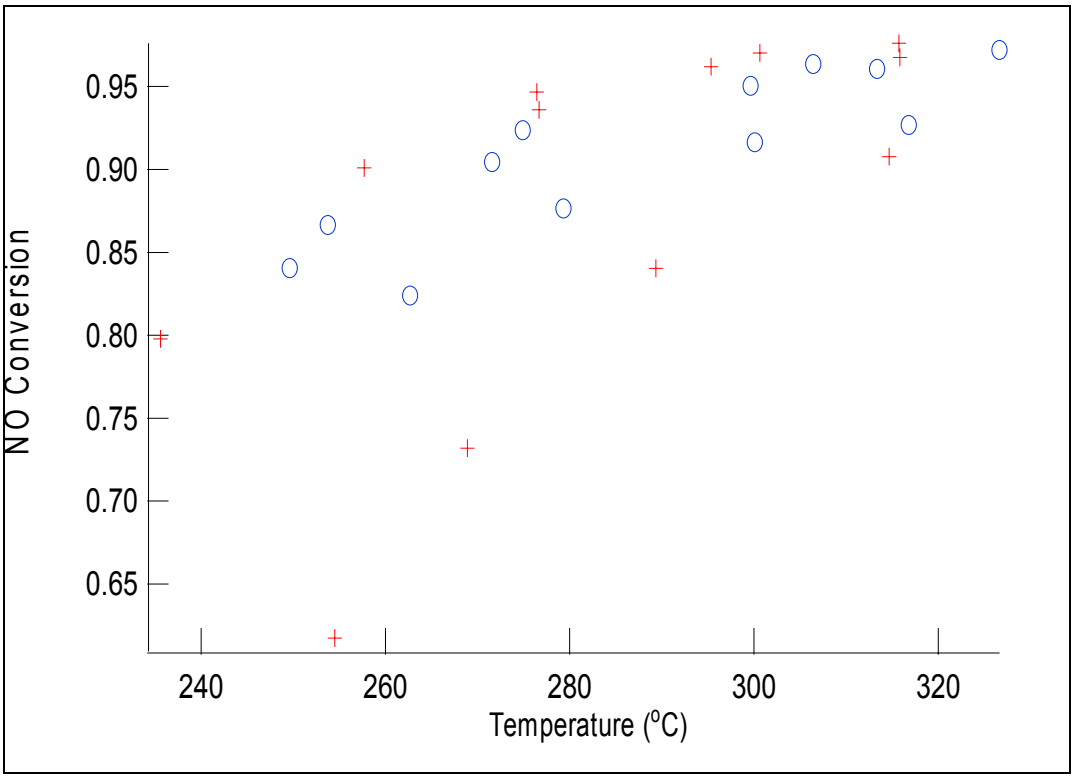

Figure 3. M3 results.

***In situ* FTIR study of NO adsorption on fresh TiO_2, 1, 2, and 5% V_2O_5/TiO_2**

During this quarter we continued a series of investigations in the in situ catalyst surface analysis experiments. Figure 4 shows the NO adsorption results on various fresh samples. During NO adsorption, 1000 ppm NO was introduced to fresh samples at room temperature for 1 hour. Results show that NO adsorbs on all samples including fresh TiO_2, 1, 2, and 5% V_2O_5/TiO_2. In Figure 4, the top spectrum represents NO adsorption on fresh TiO_2, the bottom one is from 5% V_2O_5/TiO_2, and the remaining spectra appear in order of increasing vanadia content from top to bottom. Comparing NO adsorption intensities on each sample, the general trend is observed that NO adsorption intensities decrease with increasing vanadia content on catalyst surface. However, within the same 1 and 2% V_2O_5/TiO_2 samples, various NO adsorption peak intensities are obtained. The reason may be that two different 1000 ppm NO mixtures were applied. The first 1000 ppm NO mixture is made from 2% NO (in helium) diluted with additional helium; this 1000 ppm NO mixture was tested with TiO_2 and 1% V_2O_5/TiO_2 (A) and 2% V_2O_5/TiO_2 (A, B). The other NO mixture is 1000 ppm NO in argon tested with 1 % V_2O_5/TiO_2 (B), 2% V_2O_5/TiO_2 (C), and 5% V_2O_5/TiO_2. Comparing NO adsorption on 1% V_2O_5/TiO_2 (A) and (B), a stronger NO adsorption is obtained from the first NO mixture (2% NO diluted in He) than from the second one (NO in argon). The same trend is observed for NO adsorption on 2% V_2O_5/TiO_2 with the two different NO mixtures. Therefore, comparison of NO adsorption on all samples directly is subject to systematic error. However, comparing 1% V_2O_5/TiO_2 (B), 2% V_2O_5/TiO_2 (C), and 5% V_2O_5/TiO_2, which are tested with the same NO mixture (1000 ppm NO in argon), NO adsorption intensities generally decrease with increasing vanadia content on catalyst surface, as shown in Figure 5. The same trend was observed by comparing NO adsorption on TiO_2, 1%

V_2O_5/TiO_2 (A), and 2% V_2O_5/TiO_2 (A) which are tested with the first NO mixture (2% NO diluted in helium), as shown in Figure 6. All results are consistent with our earlier suggestion that NO and vanadia compete for the same surface site, the OH group.

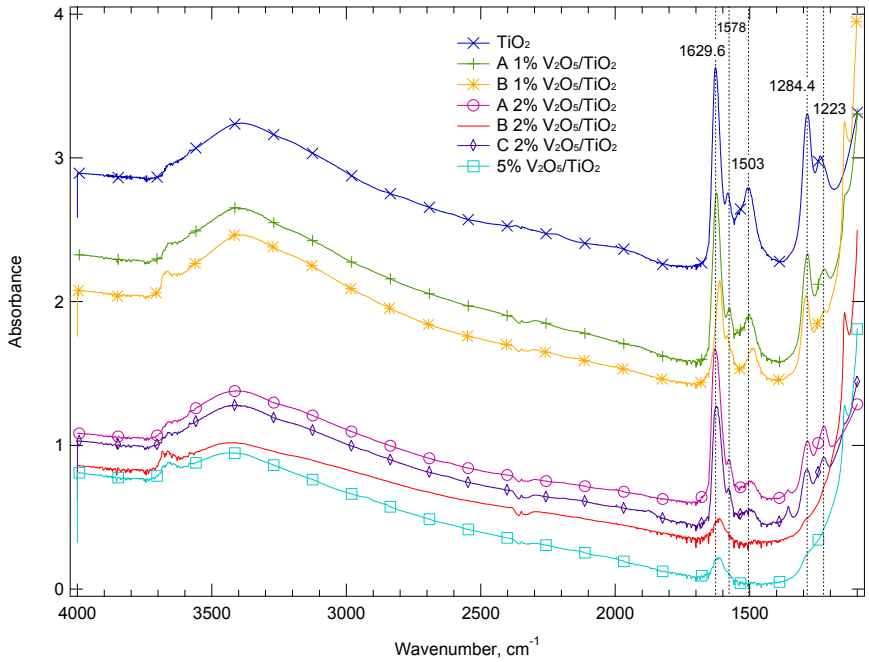

Figure 4. NO adsorption on different vanadia content (0, 1, 2, and 5%) fresh samples at room temperature.

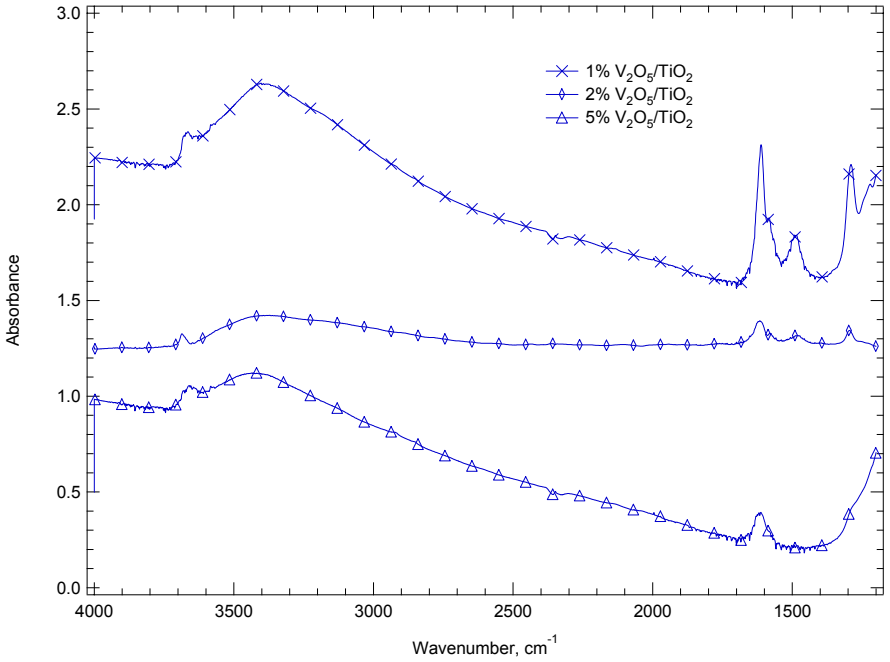

Figure 5. 1000 ppm NO in argon adsorption on 1, 2, and 5% V_2O_5/TiO_2 at room temperature.

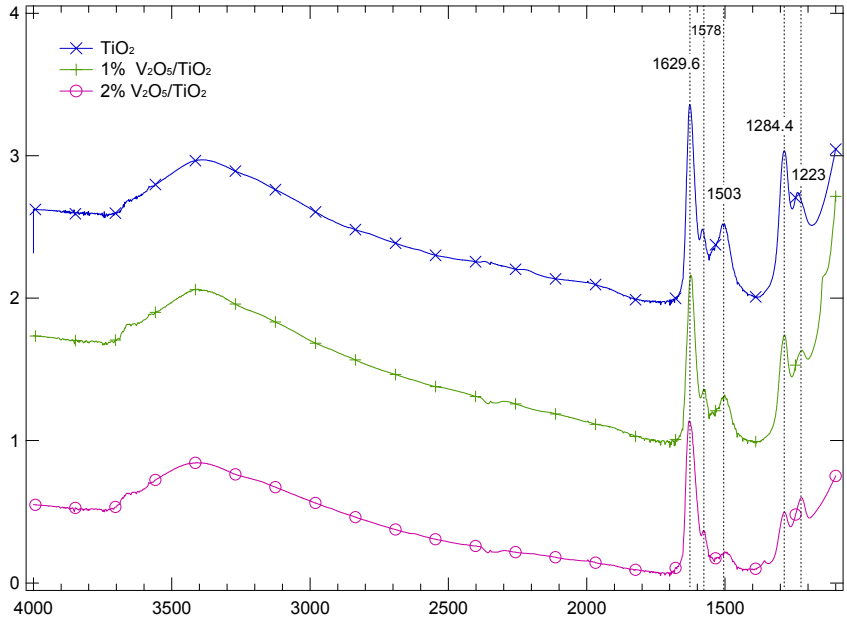

Figure 6. 1000 ppm NO in helium mixture adsorption on TiO_2, 1 and 2% V_2O_5/TiO_2 at room temperature.

The effect of sulfate on NO adsorption, as reported earlier, appears again here to establish context for the remaining discussion. Figure 7 shows the NO adsorption on fresh, lightly sulfated, and 24-hour sulfated 1% V_2O_5/TiO_2. NO adsorption peaks on the fresh 1% V_2O_5/TiO_2 catalyst are intense, but decrease with increasing sulfation time. This indicates that sulfate suppresses NO adsorption by occupying similar surface sites as NO. Therefore, both vanadia and sulfate suppress NO adsorption. In addition, vanadia tends to decrease sulfate content on catalyst surfaces as sulfate does not form on vanadia sites but rather on titania sites, as has been thoroughly documented in previous reports. All these results suggest that the OH groups on the titania surfaces are the site for NO adsorption, vanadia interaction with titania support, and sulfate interaction with the catalyst.

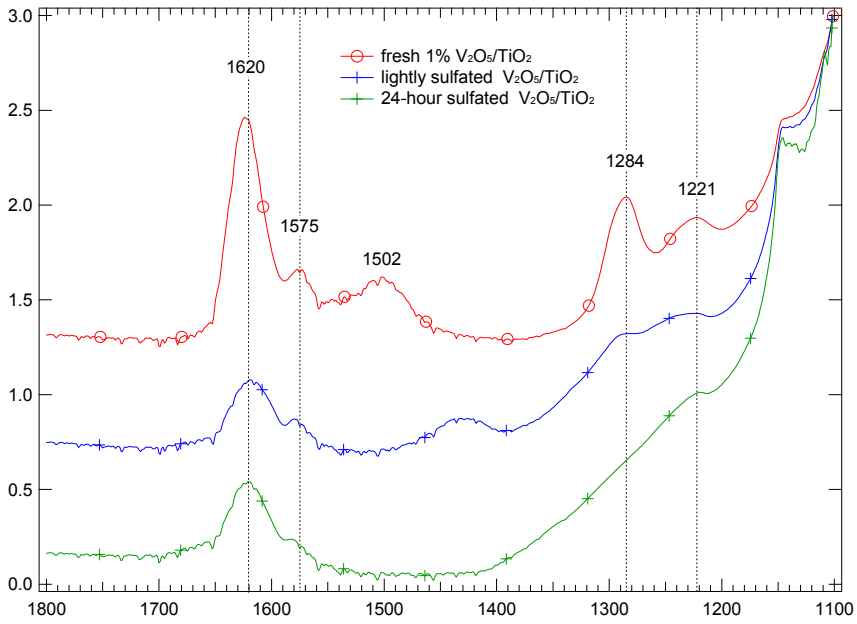

Figure 7. Comparison of NO adsorption on fresh, lightly sulfated, and 24-hour sulfated 1% V_2O_5/TiO_2.

NO reduction activity test with MS

During this quarter, conversion and kinetic activity data derived from the in situ reactor and mass spectrometer provided consistent mechanistic indications of SCR activity. These investigations involved 700 ppm NH_3 and NO, 5% O_2, and helium (balance). A total of three flow rates (93, 121, and 187 ml/min) provided a range of space velocities. The temperature ranged from 250 ˚C to 350 ˚C.

Pore diffusion limitation

SCR tests on 5 and 2% V_2O_5/TiO_2 catalysts at 350 ˚C resulted in NO conversions of about 80% and 72% respectively, which indicates that increasing vanadia content enhances NO reduction activity. However, at conversions as high as 80 and 72%, pore diffusion resistance could be dominant. For example, the calculated Thiele modulus (M_T) for 5% V_2O_5/TiO_2 is 1.06,

exceeding the 0.4 upper limit for M_T customarily accepted for negligible pore diffusion resistance. In addition, the Weisz modulus (M_W) for 5% V_2O_5/TiO_2 is 1.13, exceeding the 0.13 upper limit for M_W customarily accepted for negligible pore diffusion resistance. Pore diffusion impacts the kinetic reaction rates in these cases. Operation in regimes without such impacts provides more accurate intrinsic kinetic data. Therefore, NO reduction was tested on 1% V_2O_5/TiO_2 at 18% conversion with temperatures of about 250 ˚C and a 30% conversion at temperatures of 300 ˚C. These conditions correspond to M_Ts of about 0.25 (250 ˚C) and 0.34 (300 ˚C), respectively. Both are smaller than 0.4. Therefore the pore diffusion effects can be neglected. These investigations follow.

Film diffusion limitation

Both calculation and experiment show that film diffusion can be neglected during SCR tests on 1% V_2O_5/TiO_2.

Film diffusion resistance is determined according to

$$K_c = \frac{1-\phi}{\phi}\left(\frac{D_{AB290}}{d_p}\right)Sh' \qquad (1)$$

ø = void fraction of packed bed

D_{AB} = gas-phase diffusivity, m^2/s

d_p = particle diameter, m

Sh' =Sherwood number

The calculated result indicates that the film resistance accounts for about 0.3% of the total resistance (combined resistance of film diffusion and kinetic resistance).

Experimentally, film diffusion investigations on SCR catalysts (1% V_2O_5/TiO_2) involved three different flow rates (93, 121, 187 ml/min). This range of space velocities in the catalyst provides significant variation in the boundary layer thickness along the catalyst surface and therefore should result in different conversions if film resistance plays a significant role in NO reduction. Similar NO conversions (17.6% at 93.3 ml/min, 18% at 121 ml/min, and 17.4% at 187ml/min at 250 ˚C) resulted from each experiment, consistent with the mathematical expectation of negligible impact of film resistance. Therefore, the following SCR reactions are investigated on 1% V_2O_5/TiO_2 catalysts with 700 ppm NH_3 and NO, 5% O_2, and helium (balance) with a total flow rate of 187 ml/min at a temperature range of 250-350 ˚C, where both film diffusion and pore diffusion resistance can be neglected. This investigation involved catalyst reacting in the intrinsic kinetic range.

During NO reduction activity tests, the NO conversion is measured by comparing the changes of NO^{30}/Ar^{38} ratio of MS signal intensity before and after reaction. NO conversion increased with time, frustrating attempts to collect repeatable data. Improved normalization of the data with one of the MS measurement parameters that measures background intensity improved the results.

Kinetic parameter calculation

During this quarter, kinetic expressions for reaction rates of NO on SCR catalyst surfaces were derived from several samples. All analyses presumed a first-order surface reaction rate expression, that is

$$\frac{d[NO]}{dt} = -K[NO] \tag{2}$$

Since NO reduction experiments did not involve film or pore diffusion, kinetic parameters depend directly on NO conversion based on the following equation:

$$K = -\frac{Q_0}{W_{cat}} \ln(1 - X) \tag{3}$$

K = reaction rate coefficient

Q_0 = total gas flow rate, ml/min

W_{cat} = catalyst weight

X = NO conversion

And also

$$K = A \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

A = pre-exponential factor

E_a = activation energy

R = gas constant 8.314 J/mol·K

T = temperature, K

A matrix of reaction rate coefficient (K) values and temperatures result from measuring NO reduction as a function of temperature. Non-linear least-squares fits of these data determine the parameters A and E_a and their confidence intervals. Figure 8 shows the estimated results of A and E_a for fresh, lightly sulfated, and fully sulfated samples.

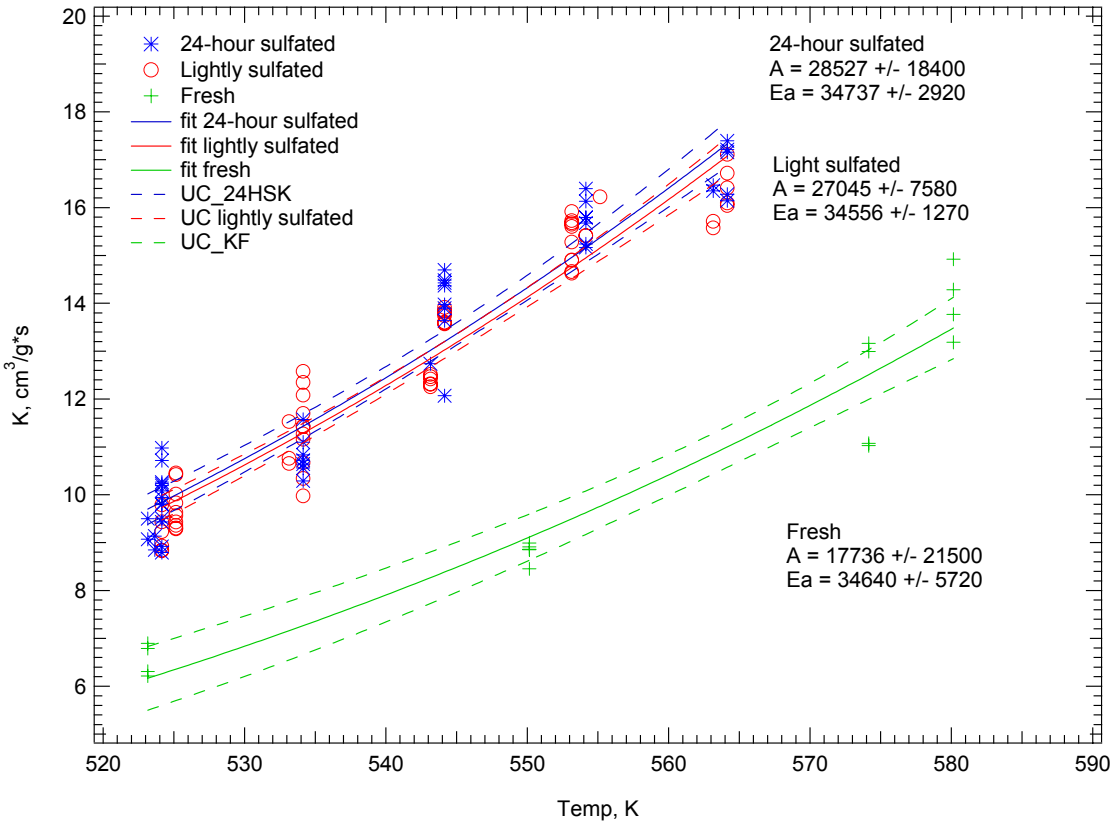

Figure 8. Kinetic parameter (A, Ea) estimations of fresh, lightly sulfated, and 24-hour sulfated 1% V_2O_5/TiO_2.

In Figure 8 the indicated symbols represent measured NO conversion data from fully (24-hour exposure) sulfated, lightly sulfated, and fresh 1% V_2O_5/TiO_2 SCR catalysts. The solid lines represent the curve fits based on the non-linear least squares algorithm for each conversion data set. The upper and lower dotted lines indicate the 95% confidence interval for the k values in each fit. They indicate that sulfated samples have statistically significant higher reaction rate coefficients than do fresh or non-sulfated samples. Typically, sulfation increases intrinsic activity by about 50% in these tests. However, there is no statistically significant difference in the reaction rate coefficient or activity between the 24-hour sulfated sample and lightly sulfated sample. Furthermore, although K increases significantly upon catalyst sulfation, the activation energy E_a remains statistically unchanged for sulfated and non-sulfated samples, with E_a = 34556~34737 J/mol. The differences in the rate coefficient arise from the pre-exponential factor, A. Results of curve fitting show that sulfated samples have larger pre-exponential factors (A = 27000-28000 cm^3/g s) than fresh samples (A = 17736 cm^3/g s). This is consistent with the in situ spectral results that indicate sulfation does not impact the vanadia grains on the catalyst. As indicated by the spectra, surface sulfation impacts the ammonia absorption on the surface, providing more opportunities for NH_3-NO interaction thus increasing the interacting frequency, which is related to A.

All of these results are generally consistent with the substantial body of data developed in this project to date. However, there is one minor inconsistency. As indicated above, there is no

statistically significant difference in either the observed reaction rate coefficient, K, or its parameters, A and E_a when comparing the lightly sulfated and 24-hour sulfated samples. In these investigations, the experimental sequence involved NO and NH_3 adsorption tests followed by SCR reactivity experiments. The spectrally determined NH_3 adsorption intensity on the 24-hour sulfated 1% V_2O_5/TiO_2 is not stronger than that on the lightly sulfated 1% V_2O_5/TiO_2, which is inconsistent with the previous results where NH_3 adsorption on 24-hour sulfated samples was stronger than that on lightly sulfated samples. The reason for the inconsistency could be due to the timing. The NH_3 and NO adsorption and SCR test on 24-hour sulfated 1% V_2O_5/TiO_2 were conducted 7 days after the 24-hour sulfation. Some surface composition changes could occur during these 7 days. Replicate experiment currently underway should resolve this minor inconsistency.

Task 4.2 Evaluation of Commercial SCR Catalysts for Power Plant Conditions

Biomass Co-firing Tests at Gadsden

The Gadsen Plant (Figure 9) is located in Gadsden, Alabama, and has two 70 MW tangentially fired boilers. It has been burning biomass as part of a three-year DOE program. Currently the plant fires switchgrass seven to eight hours per day, five days a week, in Unit 2. The switchgrass is ground and fed pneumatically into two corners of the boiler, just below the topmost coal port. The switchgrass is fired at 2.5 tons per hour, or about 5% on an energy input basis.

Figure 9. Plant Gadsden.

The difficulty in running switchgrass for extended periods of time on Unit 2, prompted Southern Company and REI to consider firing sawdust on Unit 1 by co-milling sawdust at about 5% weight basis. The plant personnel believe that they could co-mill 5% sawdust twenty-four hours

per day. This would have the advantage of longer exposure times for the catalysts to biomass and a fairly steady fuel source. The disadvantage is that the amount of biomass would be small (2-3% of the fuel on an energy basis).

Last quarter, the ammonia delivery manifold was refabricated out of stainless steel. The eyewash and shower were installed in the fan room early in the quarter. After this, the ammonia tanks were installed. The reactor started up the week of November 15, 2004.

Fuel samples (coal plus sawdust) were taken from the inlet to the pulverizer. Table 2 gives the composition of the ash from the fuel blend. (The coal ultimate analysis will be included in the next quarterly report.) The ash is low in sodium and very low in calcium. However, the potassium content (2.56 wt%) is significant.

Table 2. Ash Composition of Coal/Biomass Mixture (Pulverizer Inlet Sample).

	Mineral Analysis of Ash
Silicon Dioxide	51.39 wt. %
Aluminum Oxide	24.68 wt. %
Titanium Dioxide	1.19 wt. %
Iron Oxide	13.77 wt. %
Calcium Oxide	0.98 wt. %
Magnesium Oxide	0.95 wt. %
Sodium Oxide	0.41 wt. %
Potassium Oxide	2.56 wt. %
Phosphorus Pentoxide	0.40 wt. %
SO_3	0.95 wt. %
Manganese Dioxide	0.04 wt. %
Barium Oxide	0.25 wt. %
Strontium Oxide	0.08 wt. %

Results and Discussion

Discussion of Corrosion Monitoring Study

Thicker end-caps for the ECN probes were designed and fabricated to prevent the warpage and failure that occurred at Gavin with the previous end-cap design. One refurbished ECN probe was successfully tested at the University of Utah combustion laboratory for three days. Improvements to the software that controls the flow of cooling air to the ECN probes were implemented to avoid the cyclical heating/cooling that occurred at Gavin. The refurbished ECN probes and improved controller software will be re-installed at Gavin next quarter.

Discussion of Laboratory Study of Catalyst Activity

Investigations of commercial catalysts exposed to flue gas streams in a slipstream reactor for nominally 2000 hours continued this quarter. The investigations indicate that the activity of these samples was essentially unchanged (possibly slightly increased) relative to the activity of the fresh, unexposed samples. Statistical analyses of the results indicate that the small changes observed in catalyst behavior were insignificant or marginally significant and that the differences were greater at low temperatures, where kinetic reaction rate impact on results becomes a larger factor in overall conversion. This result is consistent with previously reported laboratory data that indicate catalyst activity increases with sulfation. Investigations of some catalyst samples proved difficult because of awkward geometric profiles of the monoliths and are still under investigation, but monoliths with rectangular channels are consistent and complete. Preliminary data (not yet graphed) with catalysts exposed for longer times (3800 hours) indicate that catalyst activity decreases relative to the fresh samples and those exposed for 2000 hours. This decrease, however, appears to be more consistent with changes in available sites or surface area rather than changes in activation energy.

In situ spectroscopic data describing NO adsorption as a function of V_2O_5 content confirm previous indications that NO and V_2O_5 compete for the same (presumably OH) sites on titania substrate. NO adsorption decreases with increasing V_2O_5 content.

Chemical reaction rate coefficients for catalysts with three levels of sulfation indicate that sulfation increases activity significantly (by 50% or more) but that the increase in activity does not involve a change in activation energy. The significant change in the pre-exponential factor is consistent with previous spectroscopic data that indicate sulfation of catalysts does not involve the vanadia (catalytic) sites but rather the substrate. Sulfation primarily leads to an increase in adsorbed ammonia, which in turn would lead to increased reaction between NO and adsorbed ammonia.

Discussion of the Slipstream Reactor Study

On November 18 and 20, 2004, an initial survey of the NO_x activity (reduction) of each catalyst was carried out. NO_x activity was computed by measuring the inlet NO_x and the outlet NO_x from each chamber using the CEM. During most of the measurements, the inlet NO_x was fairly stable.

The O_2-content of the flue gas was 3 to 4% for the sample chambers. Certain inlet measurements showed very high O_2, which indicated a leak in the sampling system. Those measurements were not used for further analysis.

Tables 3 and 4 summarize the NO_x data. Inlet NO_x values are corrected to 3% O_2 (dry basis). The ammonia was computed on a wet basis and the NH_3/NO ratio is computed on this basis. Space velocity was computed at 32 ^oF.

Figure 10 illustrates the NO_x reduction as a function of space velocity. Catalysts C1, C2, C5 and C6 are honeycomb catalysts; catalysts C3 and C4 are plate catalysts. The temperature of the catalysts was low, circa 550 ^oF. The NH_3/NO ratio was about 1.1, which was high enough to ensure that the ammonia does not limit the reduction reaction. NO_x reductions were high for all catalysts except the BYU catalyst (C1).

Table 3. NO_x Data and Activity from 11-18-04.

Sample	Time	Average inlet NO_x (3% O_2, dry)	NO_x reduction	Total flow, scfm	NH_3, ppm	NH_3/NO (act. Basis)	T-average, F	SV, hr^{-1}
INLET	18:28-18:47	445		131	430	1.03	547	
ONE	18:49-18:52	451	21.85%	130	431	1.02	548	3,735
TWO	18:54-18:56	451	65.70%	126	444	1.05	546	8,499
ONE	18:58-19:01	451	72.13%	125	449	1.06	547	3,714
INLET	19:05-19:07	457		125	451	1.05	547	
FOUR	19:09-19:12	445	91.02%	124	452	1.08	550	3,296
FIVE	19:13-19:17	445	89.25%	125	449	1.07	537	5,699
SIX	19:18-19:21	445	82.08%	127	443	1.06	536	4,505
INLET	19:25-19:28	433		126	447	1.10	544	
THREE	19:30-19:33	433	96.82%	126	445	1.09	562	2,187
TWO	19:34-19:37	433	65.40%	126	445	1.09	543	8,502

Table 4. NO_x Data and Activity from 11-20-04.

Sample	Time	Average inlet NO_x (3% O_2, dry)	NO_x reduction	Total flow, scfm	NH_3, ppm	NH_3/NO (act. Basis)	T-average, F	SV, hr^{-1}
INLET	8:17-8:19	416		100	413	1.06	548	
ONE	8:21-8:24	408	20.59%	100	417	1.09	550	2,987
TWO	8:26-9:29	408	81.82%	100	414	1.08	543	4,865
THREE	8:30-8:33	408	96.95%	96	432	1.13	567	2,147
INLET	8:37-8:40	401		94	441	1.17	549	
FOUR	8:41-8:44	404	96.54%	94	442	1.17	550	2,339
FIVE	8:46-8:49	404	93.56%	94	443	1.17	534	3,455
SIX	8:51-8:53	404	78.24%	94	443	1.17	539	4,972
INLET	8:58-9:01	408		94	443	1.15	548	
THREE	9:02-9:05	412	96.72%	95	438	1.13	565	2,120
TWO	9:07-9:10	412	81.75%	95	437	1.13	543	4,810
ONE	9:12-9:14	412	25.43%	91	458	1.18	548	2,770
INLET	9:18-9:21	417		90	462	1.18	546	
FOUR	9:23-9:25	417	97.50%	88	474	1.21	547	2,137
FIVE	9:27-9:30	417	95.70%	87	477	1.22	532	3,284
SIX	9:32-9:35	417	81.52%	87	476	1.21	535	4,553
ONE	9:44-9:46	417	20.09%	94	401	1.02	546	2,797
TWO	9:48-9:51	417	81.70%	95	400	1.02	540	4,679
THREE	9:53-9:56	417	97.69%	88	431	1.10	560	1,966
FOUR	10:04-10:07	417	97.47%	86	448	1.14	543	2,092
FIVE	10:08-10:11	417	96.01%	86	447	1.14	528	2,998
SIX	10:13-10:16	417	86.28%	88	437	1.11	533	4,629
ONE	10:25-10:28	417	18.84%	89	411	1.05	544	2,712
TWO	10:29-10:32	417	79.00%	90	408	1.04	537	4,573

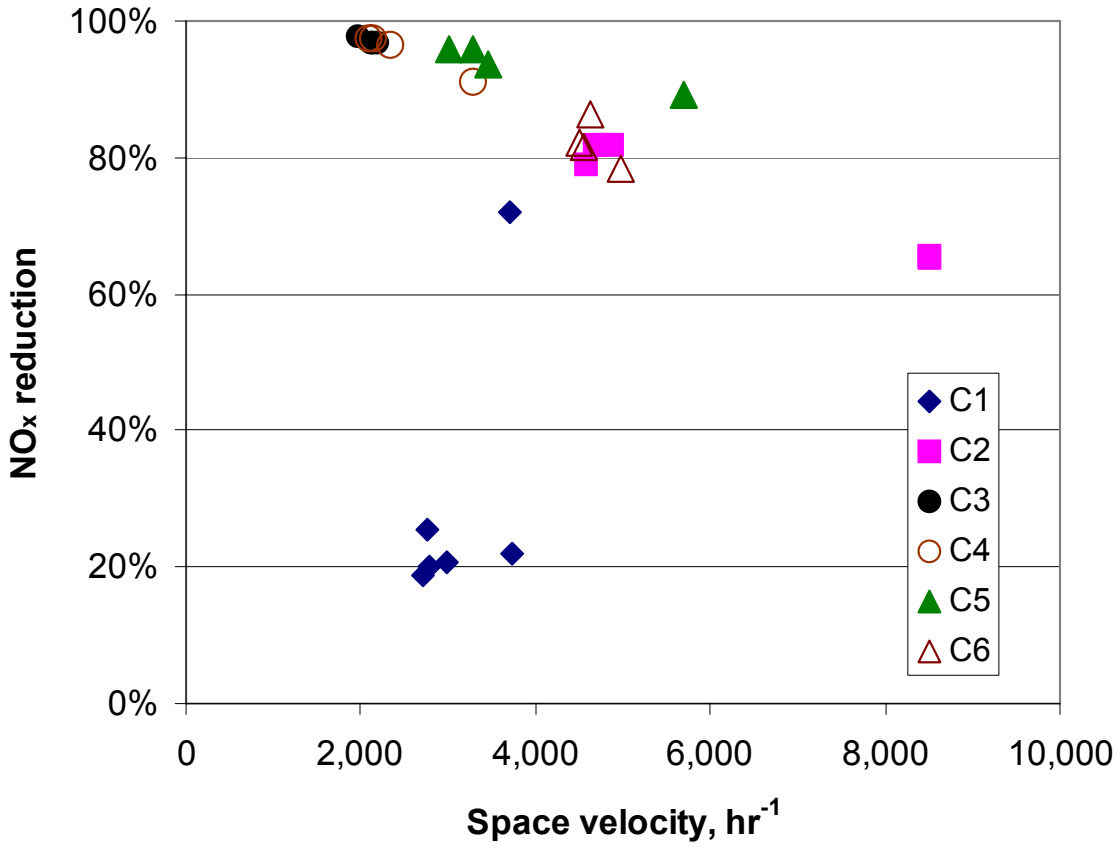

Figure 10. NO_x activity from 11/18/04 and 11/20/04 as a function of space velocity at a temperature of 550°F, NH_3/NO = 1.1.

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Conclusions

Good progress has been made on several fronts during the last three months. In particular:

- Thicker end-caps for the ECN probes were designed and fabricated to prevent the warpage and failure that occurred at Gavin with the previous design.
- One refurbished ECN probe with the thicker end-cap was tested at the University of Utah combustion laboratory for three days. The cyclical heating/cooling behavior that led to the failure of the end-caps at Gavin was not observed.
- Improvements to the software that controls the flow of cooling air to the ECN probes have been implemented.
- Safety equipment for ammonia was installed for the SCR slipstream reactor at Plant Gadsden. The reactor accumulated ~1400 hours of operation during the last performance period. A preliminary assessment of NO_x activity was made.
- Laboratory investigations at BYU of the catalysts exposed for 2000 hours to flue gas indicated that the activity of these samples was essentially unchanged (possibly slightly increased) relative to the activity of the fresh, unexposed samples. Preliminary data (not yet graphed) with catalysts exposed for longer times (3800 hours) indicated that catalyst activity decreases relative to the fresh samples and those exposed for 2000 hours.
- In situ spectroscopic data indicate that sulfation of the catalyst increases activity significantly (by 50% or more). Sulfation primarily leads to an increase in adsorbed ammonia, which in turn would lead to increased reaction between NO and adsorbed ammonia.

Plans for Next Quarter

Corrosion probe activity for the next quarter will focus on the following:

- Complete refurbishing of all ECN corrosion probes with thicker end caps.
- Reinstall all probes in Gavin and continue corrosion measurements.
- Perform profilometry analysis on selected sensor elements.
- Begin ECN corrosion data analysis.
- Continue analysis of the KEMA coupons.

Activity at BYU next quarter will focus on the following:

- Laboratory testing of catalysts exposed in the slipstream reactor.

SCR slipstream activity for the next quarter will focus on the following:

- Complete testing of catalysts in slipstream reactor and send catalysts to BYU for analysis.

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References

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